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Crystalline Ultrasmooth Self-Assembled Monolayers of Alkylsilanes for Organic Field-Effect Transistors

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Abstract: Crystalline self-assembled monolayers (SAMs) of organosilane compounds such as octadecyltrimethoxysilane (OTMS) and octadecyltrichlorosilane (OTCS) were deposited by a simple, spin-casting technique onto Si/SiO_2 substrates. Fabrication of the OTMS SAMs and characterization using ellipsometry, contact angle, atomic force microscopy (AFM), grazing angle attenuated total reflectance Fourier transform infrared (GATR-FTIR) spectroscopy and grazing incidence X-ray diffraction (GIXD) are described. The characterization confirms that these monolayers exhibit a well-packed crystalline phase and a remarkably high degree of smoothness. Semiconductors deposited by vapor deposition onto the crystalline OTS SAM grow in a favorable two-dimensional layered growth manner which is generally preferred morphologically for high charge carrier transport. On the OTMS SAM treated dielectric, pentacene OFETs showed hole mobilities as high as 3.0 $cm^2/V\cdot s$, while electron mobilities as high as 5.3 $cm^2/V\cdot s$ were demonstrated for C_{60}.

Introduction

Many linear alkyl derivatives, such as alkylthiols and alkylsilanes, have been used to modify the chemical and/or physical properties of surfaces. These molecules form self-assembled monolayers (SAMs) on the surface by physical adsorption or covalent bonding of the headgroup to the substrate and are further stabilized by attractive van der Waals packing of the alkyl chains. These SAMs have been widely investigated with particular attention to systems like thiols on gold or silver, silanes on SiO_2, phosphonic acids on Al_2O_3 and carboxylic acids on metal oxides.[1] Careful control and engineering of the SAM composition and morphology is important for many applications.[1−5]

Octadecylsilanes (OTS), such as octadecyltrimethoxysilane (OTMS) and octadecyltrichlorosilane (OTCS), have been extensively used to modify the SiO_2 dielectric surface in organic field-effect transistors (OFETs) and such modifications usually result in an increased charge carrier mobility for a variety of vacuum-deposited and solution-cast organic semiconductors.[6] OTS has been shown to reduce dielectric surface traps such as interfacial trapped water, and to tune surface energy and control surface roughness.[7,8] This modification has been used on the dielectric surface of bottom-gated OFETs because the nucleation and growth behavior of the organic semiconductors is dramatically influenced by composition and quality of the dielectric surface.[7,8] For high charge carrier transport, two-dimensional (2D) growth is preferred over three-dimensional (3D) or island growth. Thin films that exhibit 3D growth at the dielectric interface tend to form severe grain boundaries during coalescence which act as trap sites that greatly reduce charge carrier mobility. Two-dimensional layer-by-layer growth gives rise to films where islands are better connected, and charge limiting traps are minimized, engendering higher current flow.[9−12]

Cho and co-workers investigated the importance of the phase of OTS (solid vs. liquid) on pentacene OFET performance.[13]

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Recently, using the Langmuir–Blodgett (LB) technique, we systematically varied the phase of OTS and investigated pentacene and C_{60} semiconductor growth and OFET performance.[14] In the LB technique, amphiphilic OTS molecules were compressed at the air–water interface, and under applied lateral pressure a 2D liquid, solid, and even a crystalline monolayer could be formed. The maximum surface pressure that can be achieved was 55 mN/m before the OTS film began to collapse and form multilayers. At a surface pressure at or exceeding 50 mN/m a dense, crystalline OTS monolayer was formed. On this crystalline OTS monolayer, hereafter referred to as LB-50, we found that the mobility for pentacene and C_{60} thin films was significantly improved over films deposited on amorphous, disordered OTS SAMs. In fact, their mobility increased systematically with the LB OTS density.[14]

The amorphous OTS SAMs are typically formed using conventional deposition methods, such as solution immersion or vapor deposition (VD). Generally VD gives rise to a smoother surface compared to solution immersion.[6,7] Silanes, especially trichlorosilanes, polymerize easily in the presence of water and form rough multilayer surfaces. In order to obtain ultrasmooth monolayers, Wang et al. applied super-dry conditions to fabricate OTCS monolayer in solution.[15] However, it took 48 h to form a full monolayer. Typically, VD is performed under vacuum, and the silane is vaporized at elevated temperature (150–200 °C). However, SAMs formed by VD usually have a low density and are disordered.[16] Compared to conventional amorphous OTS SAMs, the crystalline OTS SAM has a higher density of terminal methyl groups which leads to improved "wetting" for a variety of organic semiconductors, i.e. 2D island growth. Unfortunately, the LB technique is not easily scalable to large area processing, and films may tear during Blodgett-transfer from the air–water interface, creating defect sites.

Recently Nie et al. reported a simple technique to fabricate well-ordered monolayers of octadecylphosphonic acid (OPA) on hydrophilic surfaces.[17] They found that such monolayers can be prepared from solutions of OPA in a nonpolar solvent with a dielectric constant between 3–5 (trichloroethylene or chloroform) by spin-coating in ambient conditions onto clean oxide surfaces, such as UV/ozone-treated silicon oxide and aluminum oxide. However, while phosphonic acid groups can easily form strong covalent bonds with aluminum oxide, they typically only physisorb onto silicon oxide. In this article, we describe a simple, spin-coating technique which allows for the deposition of a smooth, crystalline OTS SAM with the same quality as the most ordered LB-50 film on silicon oxide. Furthermore, we show that the crystalline OTS SAMs serve as excellent dielectric surface modification layers for OFETs, resulting in very high charge carrier mobilities in a large variety of organic semiconductors.

Results and Discussion

Crystalline OTS Monolayer Deposition and Characterization. Nie et al. used nonpolar solvents with a dielectric constant (ε) around 4, such as trichloroethylene (TCE) or chloroform, to form ordered OPA SAMs on UV/ozone-treated hydrophilic oxide surfaces. They hypothesized that ordered OPA monolayers were formed due to the preferential solubility of the hydrophobic tail group in the solvent and the strong interaction of the polar headgroup with the hydrophilic substrate surface. They found that the dielectric constant of the solvent is crucial to ensure uniform full coverage of OPA SAM. Only a small range of solvent polarity results in significant ordering of the polar OPA headgroups on the substrate surface. We tested solvents with a variety of dielectric constants (ε), and the corresponding SAM AFM images are shown in Figure 1. The films from hexane ($\varepsilon = 1.89$), toluene ($\varepsilon = 2.38$), and dichloromethane ($\varepsilon = 8.9$) gave rise to polymerized multilayer OTMS films that could not be removed by sonication to give a smooth monolayer (Figure 1). On the other hand good-quality monolayers were deposited from chlorobenzene ($\varepsilon = 5.62$) and trichloroethylene (TCE, $\varepsilon = 3.42$). We found that for the formation of a crystalline OTS SAM the range of solvent dielectric constants roughly needs to be the same range as reported by Nie. et al.[17] The proposed formation of an ordered OTS SAM based on the mechanism reported for OPA is illustrated in Figure 2. For OPA, when the solvent dielectric constant is significantly greater than 5, the phosphonic acids start to interact more strongly with the solvent, thus disrupting the self-assembly at the substrate–solution interface. However, when the dielectric constant of the solvent is lower than 3, OPA molecules tend to make reverse micelles in solution, which gives rise to incomplete coverage of the OPA SAM. Since alkanesilanes have similar molecular structures, i.e. the nonpolar alkyl chain and the polar headgroup, we believe the same mechanism applies here. Therefore, on the basis of the above experimental results, TCE was used as solvent for all alkylsilanes in this study.

In addition to the solvent, the silane solution concentration was also found to be critical for the quality of the SAM film. At low concentrations (<1 mM), incomplete monolayers with isolated islands were formed (Figure 3a). At higher concentrations (>5 mM), multilayers were formed (Figure 3c). Several spin-casting speeds were tested, and 3000 rpm was found to give the best results. After spin-casting, the substrates were exposed to ammonia or hydrochloric acid vapor for 10 hours at room temperature to accelerate hydrolysis of alkylsilanes and to promote bonding to SiO_2 surface.

Following the acidic or basic vapor treatment, the substrate was then rinsed or sonicated with solvents to remove any multilayers. A shorter annealing time should be possible if the concentration of acid (or base) and/or the temperature is optimized. If the films did not undergo acid or base treatment, the polymerization and bonding to the surface were incomplete, and the films were easily dissolved or delaminated by organic solvents. The typical morphology of an OTMS monolayer deposited from optimized conditions is shown in Figure 4. It can be seen that the surface of the OTMS monolayer is very smooth and shows a root-mean-square (rms) roughness of 0.1–0.2 nm over large areas (25 μm^2). This surface produced by our technique is smoother compared to silane SAMs formed

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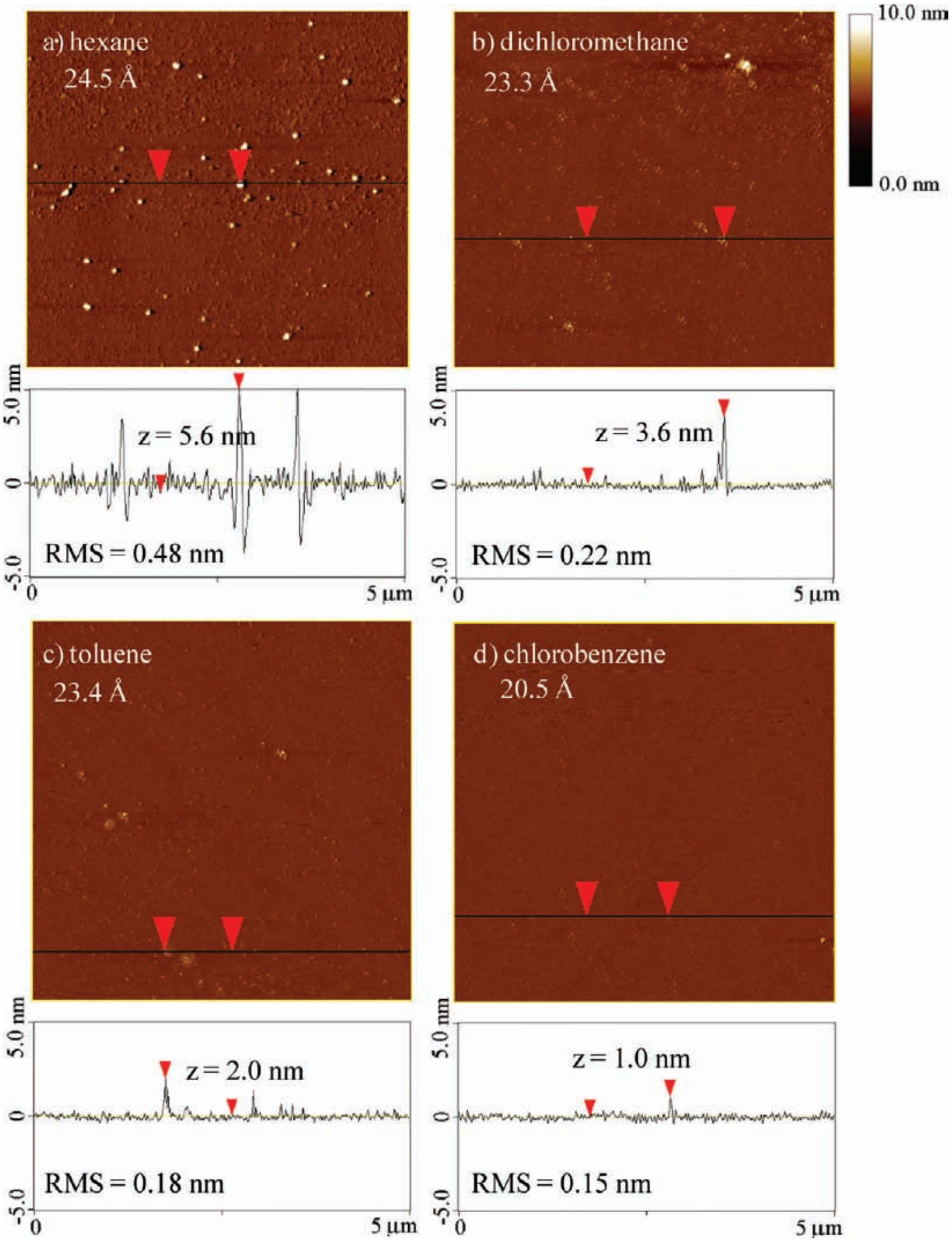

Figure 1. AFM images and line profiles of OTMS monolayers spin-cast from (a) hexane, (b) dichloromethane, (c) toluene, and (d) chlorobenzene solutions. The scan area and the height scale of every image are 5 × 5 μm^2 and 0−10.0 nm. *Z* value shows vertical distance between triangles.

by vapor or solution deposition.[14,15,23] The second and subsequent layers are not covalently bound to the surface and can be removed by rinsing or sonication. In the case of excessive multilayer formation, the multilayers were easily removed by gently wiping the surface with a toluene-soaked swab.

There was negligible difference in the film quality annealed by acid (HCl) or base (NH_4OH) vapor-catalyzed hydrolysis. Both types of films exhibited similar rms roughness (∼0.1−0.2 nm), and both formed crystalline OTS monolayers as confirmed by grazing incidence X-ray diffraction (GIXD). The pentacene FET performance (tested for over 40 transistors) was also similar on both. When trichlorosilane compounds, such as OTCS were used, they also formed smooth monolayers, but small amounts of polymerized aggregates were sometimes observed by AFM due to the very high reactivity of the trichlorosilane headgroup with moisture. However, the polymerized particles could be removed by sonication or wiping with a cleaning swab wetted with toluene.

Molecules with various alkyl chain lengths, such as butyltrimethoxysilane (BTMS), octyltrimethoxysilane (Octyl-TMS),

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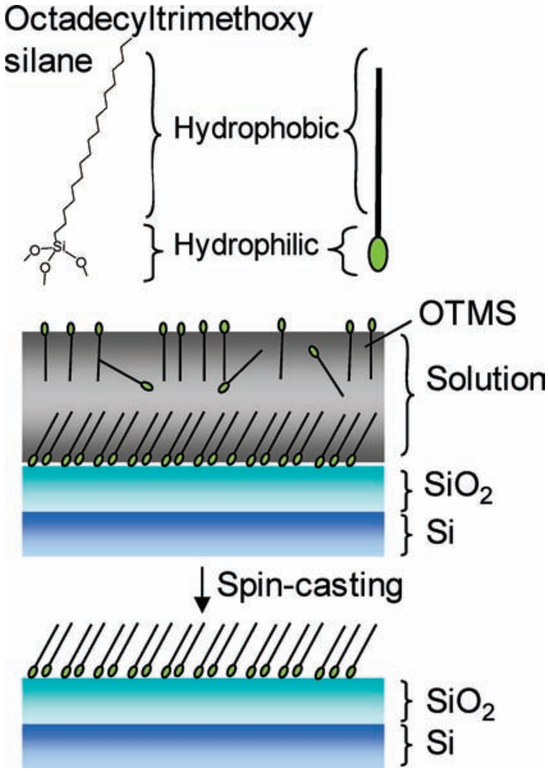

Figure 2. Schematic illustration of OTMS deposition by spin-casting is based on the mechanism proposed by Nie et. al (ref 1).

and dodecyltriethoxysilane (DTES), were also deposited by our spin-casting technique followed by NH_4OH vapor treatment. We found the difference in polarity between the side chain and the silane group to be vital for formation of good, dense monolayers: e.g. longer alkyl chain silanes formed better films than shorter alkyl chains. The theoretical molecular lengths, ellipsometric thickness on SiO_2/Si wafers, and water contact angles of each sample are summarized in Table 1. All the molecules except BTMS showed shorter extended lengths then their molecular lengths, indicating they may be tilting. However, for OTMS the GIXD data indicate that the molecules are standing up vertically, i.e. there was no evidence of the molecules tilting. The incongruence in the ellipsometric and GIXD data for OTMS is likely due to the difficulty in accurately predicting refractive indices of monolayers on surfaces. The fact the BTMS height was larger than the calculated estimated molecular length may be due to experimental inaccuracies with measuring very thin films. BTMS and Octyl-TMS SAMs showed low static water contact angles. Much better SAM surface coverage and higher water contact angle were observed for DTES (Table 1). As the alkyl chain length increases, the film coverage improves due to increased van der Waals interactions between neighboring molecules.[22] An increase in contact angle without simultaneous increase in roughness is indicative of closer packing of the alkyl chains and a decrease in surface free energy. The contact angles of DTES and OTMS SAMs are similar to those reported previously for smooth alkanes.[17,23,24]

Additional characterization of spin-cast OTS films were carried out using static water contact angle, grazing-angle total reflectance Fourier transform infrared spectroscopy (GATR-FTIR), and ellipsometry. The GATR-FTIR spectrum of the spin-cast OTS film, the LB-50 film, and the amorphous VD OTS film are shown in Figure 5. GATR-FTIR can be used to investigate monolayer density and ordering. The integrated area under the absorption curve is proportional to the monolayer density. The peak positions are indicative of the ordering and density of the monolayer. If the peak absorption shifts to lower wavenumbers, the SAM is more ordered.[14,27] We previously discussed the phase of OTMS monolayers deposited by LB technique under different surface pressures.[14] Here we compare the spin-cast OTMS films from this study to those prepared by the LB technique.[27] The most compressed and highly ordered LB film (surface pressure $\Pi = 50$ mN/m) and spin-cast film showed similar GATR-FTIR spectra, which indicates that the spin-cast film has a high degree of order and its mean molecular area is about 20 Å^2/molecule.[24]

In order to determine if the spin-cast monolayer was indeed crystalline, GIXD experiments were performed. GIXD is an ideal tool to investigate the structure of ordered monolayers. In this technique, the thin films are exposed to high intensity synchrotron X-rays under a very shallow angle (~0.1°) so that the X-rays penetrate and are scattered not only out-of-plane (perpendicular to the substrate) but also in-plane. Thus for a monolayer, where only in-plane ordering exists, GIXD allows one to determine if in-fact the monolayer is crystalline. If the monolayer is crystalline, it satisfies the Bragg-condition in-plane so that a Bragg rod is observed. Figure 8d shows the GIXD images of the spin-cast OTMS monolayer. The diffraction peak of the spin-cast OTMS is unambiguous evidence of the crystalline order of the OTMS monolayer. The diffraction pattern is virtually identical to that of the highest density LB film (50 mN/m). From the diffractogram we calculated the hexagonal lattice constant of the crystalline OTMS as 4.2 Å, which agrees with previous reports for crystalline OTS.[24] Formation of dense and crystalline packing by spin-casting is unusual for alkylsilanes since common deposition methods usually result in disordered or multilayer films.

Field-Effect Transistors (FETs). Top-contact OFETs with various organic semiconductors were fabricated and FET performance was tested to determine the efficacy of the crystalline spin-cast OTS SAM as a dielectric surface modification layer. Table 2 shows charge carrier mobility, on/off ratio, and threshold voltage for OFETs with either pentacene (p-channel) or C_{60} (n-channel) active layers on spin-cast OTS and conventional VD OTS.[6,27] Pentacene and C_{60} were chosen for p-type and n-type semiconductors respectively, because they possess exceptionally high field-effect mobilities and are among the most extensively studied organic semiconductors.[6.14] On spin-cast OTS SAMs, pentacene and C_{60} OFETs exhibited mobilities as high as 3.0 and 5.1 cm^2/V·s, (Figure 6) respectively, while much poorer mobilities of 0.56 and 0.27 cm^2/V·sec were obtained on vapor-deposited OTS SAMs. The mobility on the crystalline OTS is among the highest reported for these two organic semiconductors.[14,26]

It is well-known that the charge transport in thin film OFETs is confined to the first few monolayers at the dielectric−semiconductor interface.[10,11] To understand the role of the OTS on the charge carrier mobility in more detail, we chose to study this

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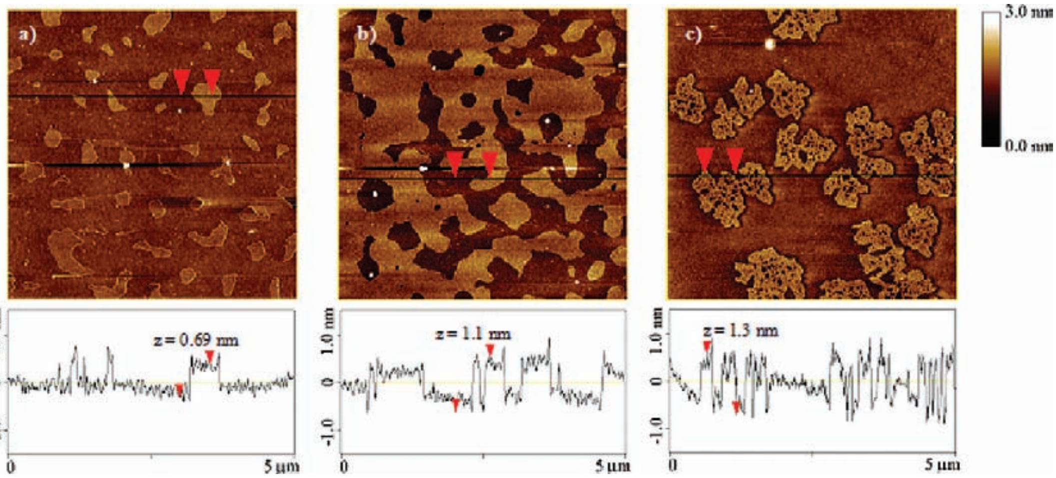

Figure 3. AFM images and line profiles of OTMS monolayer films by casting in TCE (a) is <1 mM, (b) is 2−3 mM, and (c) is >3 mM.

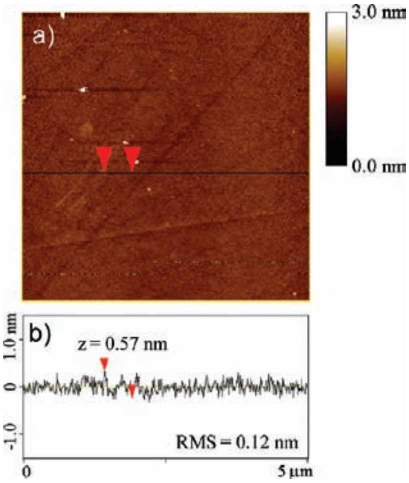

Figure 4. AFM image and line profile of an OTMS monolayer deposited by spin-casting technique from optimized conditions. The scan area is 5 × 5 μm^2. Z value shows vertical distance between triangles.

Table 1. Ellipsometric Thickness and Contact Angle of Water of Alkanesilane SAMs Deposited on Si/SiO$_2$ Wafers by Spin-Cast Technique and Followed by Ammonia Treatment

	BTMS	Octyl-TMS	DTES	OTMS
calculated thickness [Å]	5.3	10.6	18.2	23.0
thickness [Å]	7.4	6.0	17.0	21.0
contact angle [deg]	75	75	105	105

critical region by depositing nominally 3 nm (∼1.5 monolayers) of pentacene onto the different OTS SAM-treated substrates. The morphology of these samples was studied by AFM and GIXD. Figure 7 shows AFM images of 3 nm pentacene deposited on spin-cast OTMS, highly ordered LB 50 OTS, and vapor OTS. Pentacene grown on vapor (disordered) OTS exhibited undesirable 3D island growth and thus formed a discontinuous film.[26−29] The AFM line profile for the pentacene grown on VD OTS shows very tall discontinuous 3D islands (Figure 8a). In contrast, the pentacene growth on the crystalline, spin-cast OTS SAMs is very different. The strong interaction between pentacene molecules and the dense methyl-terminated substrate resulted in larger 2D grains and a more continuous film with less severe energetic trap states. More in-depth comparison and analysis of semiconductor growth mode on disordered vs crystalline OTS are given in a previous report.[14] It is important to note that AFM was taken immediately after deposition to avoid film reorganization or degradation.

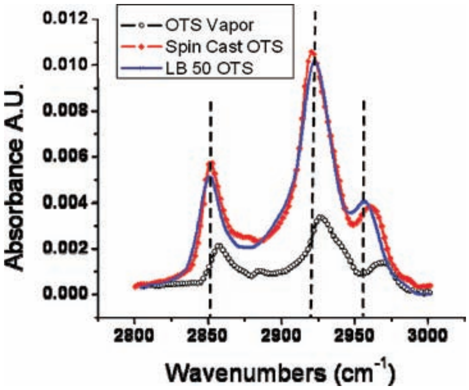

Figure 5. GATR-FTIR spectrum of the most ordered LB film (with a molecular density of ∼1 molecule/20 Å^2 from ref 14), the spin-cast OTS, and OTS-vapor. The area under the absorption curve can be used to estimate the molecular density. The area under absorption peaks for the LB 50 film and the OTS spin-cast films indicates they are of similar density. The absorbance of the OTS-vapor film is much less which further asserts that it is less dense and less ordered than the crystalline spin-cast and LB OTS films.

The characteristic pentacene (11 L), (02 L), and (12 L) in-plane Bragg rods are seen in the GIXD spectra shown in Figure 8. On the crystalline OTS (Figure 8b and c), the diffraction from the OTS SAM can be clearly observed between the (11 L) and (02 L) pentacene peaks. The lattice constants of pentacene (a = 5.93 Å, b = 7.58 Å, $\gamma \approx 90°$) extracted from the diffraction peaks were nearly identical for both the disordered and crystalline OTS and are similar to those reported for pentacene grown on alkylsilanes.[29,30] The pentacene GIXD spectra (position of peaks in Q_{xy} and Q_z) are also similar on all the OTS surfaces. This suggests that the difference in mobility on different OTS surfaces is not due to different pentacene packing motifs.[31,32] It is also interesting to note that there is an additional diffraction peak at Q_{xy} =1.6 on vapor OTS (Figure

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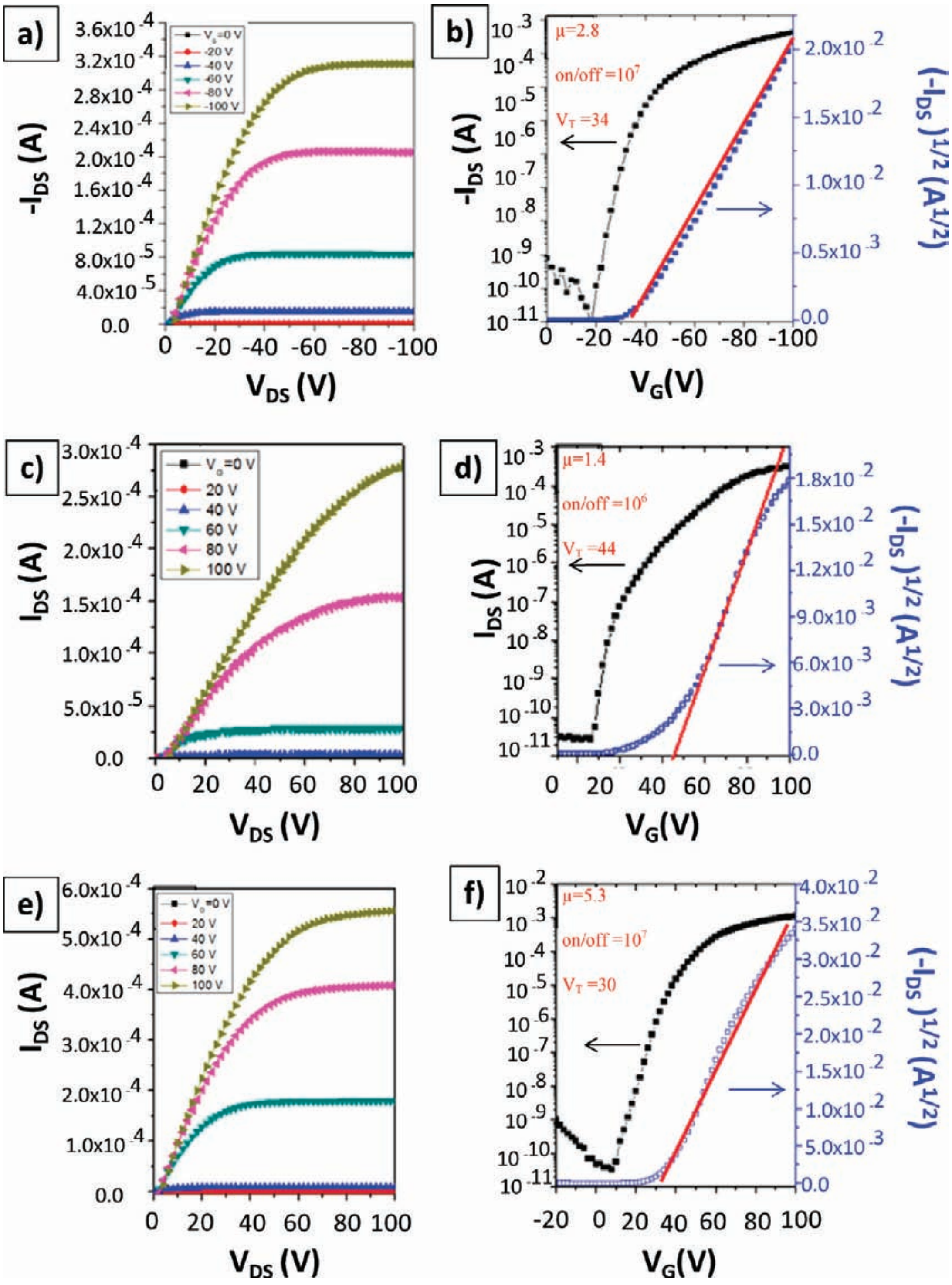

Figure 6. Representative current−voltage (IV) curves for OFETs with spin-cast OTS dielectric surface modification layer. (a) Pentacene output IVs, (b) pentacene transfer IVs, (c) PTCDI-C_4F_4 output IVs, (d) PTCDI-C_4F_4 transfer IVs, (e) C_{60} output IVs, (f) C_{60} transfer IVs. The inset in the transfer curves show the mobility μ ($cm^2/(V\ s)$), on/off, and the threshold voltage V_T (V). The red lines in the transfer plots indicate the slope used to calculate mobility. The thickness of the organic semiconductor is about 45 nm measured by a quartz crystal microbalance during deposition.

Table 2. FET Performances of Semiconductors Deposited on Both Spin-Cast OTMS and Vapor Deposited OTS

	pentacene		C_{60}	
OTS	spin-cast	vapor	spin-cast	vapor
μ [$cm^2/V\cdot s$]	2.8 ± 0.2	0.52 ± 0.04	4.7 ± 0.41	0.27 ± 0.15
I_{on}/I_{off} [-]	$(3.2 \pm 0.8) \times 10^6$	$(1.6 \pm 0.2) \times 10^5$	$(3.5 \pm 1.2) \times 10^7$	$(7.5 \pm 6.3) \times 10^5$
V_{th} [V]	-29.5 ± 6.5	9.5 ± 0.7	35.6 ± 6.3	39.8 ± 7.5

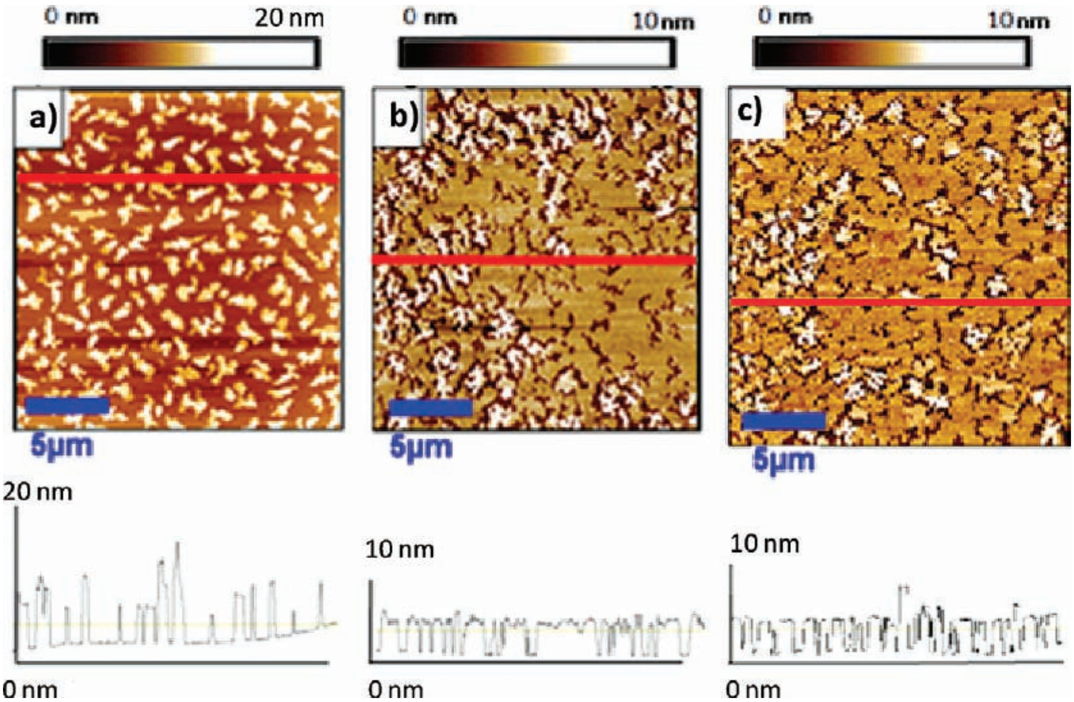

Figure 7. AFM images of 3 nm, and pentacene deposited on (a) OTS-vapor (b) spin-cast OTS, and (c) LB 50 OTS.

8a) which corresponds to a portion of the film exhibiting the bulk pentacene phase. This partial 3D growth on vapor OTS is consistent with thin film morphology investigated by the AFM (Figure 7). In principle, the full-width at half max (fwhm) of the diffraction peaks can be used to gauge the crystalline quality of the pentacene on various OTS surfaces, but for all the films studied, the fwhm was resolution limited (due to sample size effects).[33]

For the typical n-channel material, C_{60}, the densely packed SAM served as an excellent dielectric modification layer and a field-effect electron mobility as high as 5.1 $cm^2/V \cdot s$ was achieved. This mobility is among the highest reported for n-channel OFETs.[34] In addition to the morphological effects on semiconductor growth, the densely packed SAM effectively passivates electron traps on SiO_2 which can also contribute to the high mobilities especially for electron transporting materials.[35] We also tested other n-channel organic semiconductors based on perylene tetracarboxylic diimide (PTCDI), which is one of the most promising n-channel candidates due to the high electron affinity and the large π-orbital overlap in the solid state. The filed-effect mobility of *N*,*N*′-bis(heptafluorobutyl)-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C4F7) increased to 1.4 $cm^2/V \cdot s$ on the spin-cast OTS compared to 0.72 $cm^2/V \cdot s$ for the OFET device prepared on vapor-treated OTS.[27] A PTCDI compound with two fluorine atoms at the core-aromatic ring also exhibited enhanced mobilities on spin-cast OTMS SAM layer (0.66 $cm^2/V \cdot s$) compared to the vapor-treated OTS (0.35 $cm^2/V \cdot s$).[36] The spin-cast OTS allowed for the observation of ambipolar transport for a variety of pentacene derivatives while they could not be observed on vapor OTS (see Supporting Information).[37,38] These results indicate that our spin-coating of OTS SAM layer is useful for the preparation of high performance n-type and ambipolar OFETs.

Conclusions

In conclusion we have developed a simple, ambient condition, solution-deposition technique to create crystalline layers of OTS on SiO_2 surfaces. Modifying the SiO_2 dielectric using a crystalline OTS layer compared to the conventional amorphous OTS resulted in much higher charge carrier mobilities for both p- and n-channel vapor deposited organic semiconductors. The improvement in performance was attributed to the more desirable 2D semiconductor growth on crystalline OTS leading to well connected highly conductive films, as opposed to 3D growth which is commonly observed on amorphous OTS. The high density and close packing of the terminal methyl groups in crystalline OTS monolayer interact favorably with the semiconductor layer initially deposited and template 2D growth. Moreover, compared to other techniques for crystalline OTS deposition, such as the Langmuir−Blodgett method, this technique is more amenable to large area processing. Although a 5 in. silicon wafer was the largest we could test, this technique should be scalable to larger areas. We are also currently investigating the applicability of this technique to other flexible substrates and dielectrics for printed electronics. We have been able to deposit the OTS SAM on conventional organic dielectric

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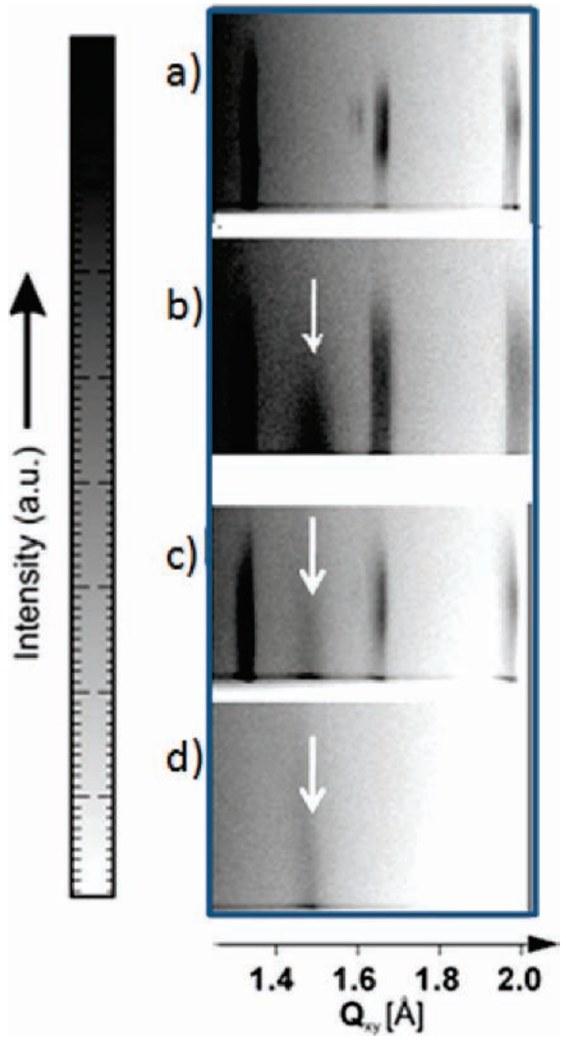

Figure 8. GIXD spectrum of 3 nm pentacene deposited on (a) OTS-vapor (note there is no diffraction from the amorphous OTS), (b) spin-cast OTS, (c) LB-50 OTS, (d) spin-cast OTS (with no pentacene) showing that, indeed, the monolayer is crystalline.

materials, such as poly(vinylphenol) (PVP) or epoxy polymers, and observed improved OTFT performance.[39] Currently we are still in the process of rigorously analyzing these monolayers to determine if they are as well ordered and crystalline as SAMs formed on silicon oxide. The formation of a crystalline OTS layer, which greatly increases performance, from a simple solution deposition process represents an important development for organic electronics.

Methods

Materials. The alkylsilane compounds, octadecyltrimethoxysilane (OTMS), octadecyltrichlorosilane (OTCS), dodecyltriethoxysilane (DTES), octyltrimethoxysilane (Octyl-TMS), and butyltrimethoxysilane (BTMS) were purchased from Gelest Inc. and used without further purification. They were stored under dry argon prior to usage and in nitrogen after usage. All solvents were purchased from Fisher Scientific. All other chemical reagents were purchased from VWR International except for ammonium hydroxide (Arista, BDH). Si wafers with 1−2 nm native oxide or 300 nm thermally grown oxide were obtained from Silicon Quest inc. They were cleaned in a piranha solution (70:30, H_2SO_4:H_2O_2 -caution highly reactive with organic compounds) and UV/ozone (Jetlight Model 4050) treatment for 10 min, followed by copious rinsing with deionized (DI) water. Pentacene and C_{60} were purchased from Sigma-Aldrich and Alfa Aesar, respectively. C_{60} (99.5% pure) was used as received, and pentacene was purified twice by zone sublimation before usage. Professor Frank Würthner from the Universität Würzburg provided the PTCDI-C_4F_4*N*,*N*′-bis(heptafluorobutyl)-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C4F7) and was sublimed prior to usage.

Self-Assembled Monolayer (SAM) Deposition. General alkanesilane deposition conditions were developed by modifying the procedure reported for octadecylphosphonic acid (OPA) monolayers on hydrophilic substrates by spin-casting.[17] For alkyl-trialkoxysilanes, the solution was dispensed onto SiO_2/Si wafers and allowed to partially self-assemble for 10 s prior to spinning coating at 3000 rpm for 10 s. The substrate was subsequently vapor annealed in ammonia or hydrochloric acid. The best conditions for crystalline OTS is the following: 3 mM OTMS solution in trichloroethylene (TCE) was cast onto a UV/ozone cleaned SiO_2/Si wafer to cover the entire surface and was allowed to partially assemble for 10 s; the substrate was then spun at 3000 rpm. Following spin-casting the substrate was put in a closed container with a small vial which containing a few millimeters of ammonium hydroxide solution (28−30% in water) for 10 h at room temperature. The substrates were then rinsed with DI water and sonicated in toluene.

Characterization. Static contact angles were measured with an Edmund Scientific goniometer and the probe fluid was milli-Q water. Ellipsometric measurements of SAMs on Si wafers with a native oxide were performed with a Sopra Bois-Columbes ellipsometer. The light source was a Physike Instrumente He−Ne laser with $\lambda = 632.8$ and the angle of incidence was 70°. The thickness of the SAM was calculated from the measured Δ and Ψ values using special integrated software (Optrel GbR) with the following parameters: air, refractive index (n_0) = 1.0; alkylsilane, $n_1 = 1.450$;[i] native silicon oxide, $n_2 = 1.460$, thickness (d) = 1.77 nm; silicon, $n_3 = 3.873$, $k = -0.016$. The SAM films were assumed to be isotropic and homogeneous.

The atomic force microscope (AFM) images of organic semiconductor thin films and the SAM-treated SiO_2/Si substrates were collected using a Digital Instruments MMAFM-2 scanning probe microscope. Tapping mode AFM was performed on the samples with a silicon tip with a frequency of 300 kHz.

The grazing angle attenuated total reflectance (GATR) spectrum was obtained using a Nicolet 6700 Fourier Transform infrared spectrometer (FTIR) using a germanium crystal.

Grazing incidence X-ray diffraction (GIXD) experiments were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11−3 with a photon energy of 12.73 keV. A 2D image plate (MAR345) with effective pixel size of 150 μm (2300 × 2300 pixels) was used to detect the diffracted X-rays. The detector was 400.15 mm from the sample center. The angle of incidence was kept fixed at 0.1° to maximize the diffracted signal and minimize the background from the substrate scattering. The GIXD data was analyzed using FIT-2D and Peakfit software programs.

FET Device Fabrication. Heavily n-doped silicon substrates with a thermally grown 300 nm silicon dioxide dielectric layer with a capacitance per unit area (*Ci*) of 10 nF/cm^2 were used as transistor substrates. For top-contact geometry, the organic semiconductors were deposited at a rate of 0.3−0.6 Å/s under a pressure of 5.0×10^{-7} Torr and a substrate temperature of 60 °C for pentacene or 110 °C for C_{60} to a final thickness of 450 Å determined by a quartz crystal monitor in the evaporation chamber. Then, gold electrodes (~40 nm in thickness) were deposited using shadow masks with a *W*/*L* of 20 (*W* = channel width, *L* = channel length), where *L* = 50−150 μm. Pentacene TFTs with channel lengths of 50 and 150 μm were both tested. For other semiconductors a 50 μm channel length was used for TFT fabrication. From our previous work contact resistances were negligible (orders of magnitude smaller)

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than channel resistances for TFTs with 50 μm channel lengths. Moreover, the difference in contact resistances for TFTs fabricated on crystalline vs amorphous OTS varied by less than 3%. This further indicates that the OTS order changes the channel conduction by influencing the semiconductor growth and morphology[14] The electrical characteristics were obtained at room temperature using a Keithley 4200 (Hewlett-Packard) semiconductor parameter analyzer in air for pentacene or under nitrogen for C_{60}. Transfer IV characteristics were obtained with a fixed source-drain voltage of −100 V for pentacene FETs and 100 V for C_{60} FETs.

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Supporting Information Available: Comparison of mobilities of several n- and p-channel organic semiconductors on amorphous, versus crystalline OTS. This material is available free of charge via the Internet at http://pubs.acs.org.

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